

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 533 239 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
01.04.1998 Bulletin 1998/14

(51) Int Cl⁶: **C11D 3/386**, C11D 17/00,
C11D 3/00, C11D 3/395

(21) Application number: **92202668.7**

(22) Date of filing: **03.09.1992**

(54) **Aqueous liquid cleaning compositions**

Wässrige flüssige Reinigungsmittelzusammensetzungen
Compositions détergentes aqueuses et liquides

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(30) Priority: **17.09.1991 GB 9119936**

(43) Date of publication of application:
24.03.1993 Bulletin 1993/12

(73) Proprietors:

- **UNILEVER N.V.**
3013 AL Rotterdam (NL)
Designated Contracting States:
CH DE ES FR IT LI NL SE
- **UNILEVER PLC**
London EC4P 4BQ (GB)
Designated Contracting States:
GB

(72) Inventor: **Tomlinson, Alan D.,**
Unilever Res. Vlaardingen Lab.
NL-3133 AT Vlaardingen (NL)

(74) Representative: **Kan, Jacob Hendrik, Dr. et al**
Unilever N.V.
Patent Division
P.O. Box 137
3130 AC Vlaardingen (NL)

(56) References cited:
DE-A- 1 940 654 **DE-A- 2 337 338**
US-A- 4 421 664

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

DescriptionTECHNICAL FIELD

This invention relates to aqueous liquid cleaning compositions comprising an enzyme and encapsulated bleach particles. In particular, it relates to enzymatic aqueous liquid cleaning compositions, especially but not exclusively adapted for use in automatic dishwashing machines, comprising an enzyme, encapsulated bleach particles and a reducing agent.

BACKGROUND OF THE INVENTION

Cleaning compositions having a combination of bleaching action and enzymatic degradation of biochemical soils, which comprise a slow release oxidant bleach composition in the form of encapsulated bleach particles which delay the appearance of the full concentration of the oxidant bleach but having the tendency to release a small deactivating amount of the oxidant, prior to the full concentration of the bleach being released, a biological soil-degrading enzyme and an amount of a chemical reducing agent effective to delay the appearance of an enzyme-deactivating concentration of oxidant bleach composition until the full concentration of the oxidant bleach composition is released, are known and described in US Patent Specification 4,421,664. The formulation of such detergent compositions in the form of a dry solid powdered or granular state presents no problem and creates substantially no difficulties with respect to enzyme stability during storage. However, if such compositions are formulated as an aqueous liquid, enzyme storage stability becomes a problem, even at milder alkaline pH values wherein enzymes are normally easier to stabilize.

In the area of "safe", i.e. mild machine dishwashing liquids, the evidence to date suggests that the incorporation of enzymes into aqueous liquids containing oxidant bleach encapsulates (either chlorine or oxygen-yielding oxidizing bleaches) may not be viable because of poor enzyme stability, caused by even a very slight leakage from the bleach encapsulates into the bulk liquid. It has been found that only 4 ppm. available chlorine is enough to quickly destroy all the amylase (an amylolytic enzyme) and about 100 ppm. available chlorine will destroy all Savinase® (a proteolytic enzyme), incorporated into a model aqueous non-phosphate machine dishwashing liquid product formulation.

Addition of a reducing agent, such as sodium sulphite, as scavenger for the oxidant as proposed in US Patent 4,421,664 does not improve the enzyme stability sufficiently enough to arrive at a commercially viable product with adequate and consistent performance of both the enzyme and the bleach. Apparently, in aqueous liquid compositions, the reducing agent is not sufficiently effective to scavenge the oxidant for a sufficient amount of time.

It is therefore an object of the present invention to improve the stability of aqueous liquid cleaning compositions comprising an enzyme and an oxidant bleach in the form of encapsulated bleach particles.

It has now surprisingly been found that the enzyme stability in such aqueous liquid cleaning compositions can be substantially improved if the composition fulfils the following two conditions, i.e. a water content of from 10% to not more than 55% by weight and containing a reducing agent in an amount of from 0.01 to 0.5% by weight.

DESCRIPTION OF THE INVENTION

Accordingly, the invention provides an improved aqueous liquid cleaning composition comprising a detergency builder, an enzyme, encapsulated bleach particles and a reducing agent, characterized in that the composition has a water content of from 10% to not more than 55% by weight, preferably not more than 50% by weight, and the reducing agent is present in an amount of from 0.01 to 0.5% by weight.

The term "aqueous liquid" used herein encompasses low-viscosity liquids to the more highly viscous liquids as well as gels and pastes, having water contents of from 10-55% by weight, preferably from 25-55% by weight, and more preferably from 35-50% by weight. Preferably, the composition of the invention is a mildly alkaline aqueous liquid.

By "mild" is meant here that the neat composition will have a pH of from 5.0 to 10.5, preferably from 6.5 to 10.5, more preferably from 8 to 9.5.

The Detergency Builder

Soluble detergency builder salts useful herein can be of the poly-valent inorganic and poly-valent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic alkaline detergency builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, triphosphates, bicarbonates and silicates. Specific examples of such salts include the sodium and potassium tetraborates, bicarbonates, carbonates, triphosphates, orthophosphates and hexametaphosphates.

Examples of suitable organic alkaline detergency builder salts are (1) water-soluble amino polyacetates, e.g. sodium and potassium ethylenediamine tetraacetates, nitrilotriacetates and N-(2-hydroxyethyl)nitrilotriacetates; (2) water-

soluble salts of phytic acid, e.g. sodium and potassium phytates; (3) water-soluble polyphosphonates, including sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium salts of methylenediphosphonic acid and the like.

Additional organic builder salts useful herein include the polycarboxylate materials described in US Patent Specification N° 2,264,103, including the water-soluble alkali metal salts of mellitic acid and citric acid, dipicolinic acid, oxydisuccinic acid and alkenyl succinates. The water-soluble salts of polycarboxylate polymers and copolymers, such as are described in US Patent Specification N° 3,308,067, are also suitable herein.

It is to be understood that, while the alkali metal salts of the foregoing inorganic and organic poly-valent anionic builder salts are preferred for use herein from an economic standpoint, the ammonium, alkanolammonium, e.g. triethanolammonium, diethanolammonium, and the like, water-soluble salts of any of the foregoing builder anions are useful herein.

Another class of suitable builders is that of the so-called water-insoluble calcium ion-exchange builder materials. Examples thereof include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best-known representatives. Other useful materials are, for example, the layered silicates, such as a product sold by Hoechst under the trade name SKS-6.

Mixtures of organic and/or inorganic builder salts can be used herein.

While any of the poly-valent builder materials are useful herein, the compositions of the invention are preferably free of phosphate builders for environmental and ecological reasons.

Preferred builders for use in the invention are sodium citrate, sodium carbonate, and sodium bicarbonate and mixtures thereof, or the potassium salts thereof. The potassium salts may be preferred for solubility reasons.

Preferably, the amount of builders in the composition is from about 5 to 60% by weight, more preferably from 25 to about 40% by weight.

The Enzymes

Enzymes are used for many purposes in various fields where biochemical reactions occur. In general, an enzyme can be described as a catalyst capable of permitting a biochemical reaction to quickly occur and can be classified according to the type of reaction they catalyze. Enzymes are characterized by a high specificity, that is to say, each enzyme can catalyze a single reaction of one substance or a very small number of closely related substances.

Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, peptidases, amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of biochemical soils and stains encountered in cleansing situations so as to remove more easily the soil or stain from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removability. Well-known and preferred examples of these enzymes are proteases, lipases and amylases.

Lipases are classified as EC class 3, hydrolases, subclass EC 3.1, preferably carboxylic ester hydrolases EC 3.1.1. An example thereof are lipases EC 3.1.1.3 with the systematic name glycerol ester hydrolases. Amylases belong to the same general class as lipases, subclass EC 3.2, especially EC 3.2.1 glucose hydrolases such as 3.2.1.1, alpha-amylase with the systematic name alpha-1,4-glucan-4-glucanohydrolase, and also 3.2.1.2, beta-amylase with the systematic name alpha-1,4-glucan maltohydrolase. Proteases belong to the same class as lipases and amylases, subclass EC 3.4, particularly EC 3.4.4 peptide peptidohydrolases such as EC 3.4.4.16 with the systematic name subtilopeptidase A.

Obviously, the foregoing classes should not be used to limit the scope of the invention. Enzymes serving different functions can also be used in the practice of this invention, the selection depending upon the composition of biochemical soil, intended purpose of a particular composition, and the availability of an enzyme to degrade or alter the soil.

Lipases, sometimes called esterases, hydrolyze fatty soils. Lipases suitable for use herein include those of animal, plant and microbiological origin. Suitable lipases are also found in many strain of bacteria and fungi. For example, lipases suitable for use herein can be derived from *Pseudomonas*, *Aspergillus*, *Pneumococcus*, *Staphylococcus*, *Toxins*, *Mycobacterium Tuberculosis*, *Mycotorula Lipolytica*, and *Sclerotinia* microorganisms, and can be made using recombinant DNA manufacturing techniques.

Suitable animal lipases are found in the body fluids and organs of many species. A preferred class of animal lipase herein is the pancreatic lipase.

Lipase can be employed in the present cleaning compositions in an amount from about 0.005% to about 10%, preferably from 0.01 to 5% of the cleaning composition, on a pure enzyme basis.

The enzymes most commonly used in machine dishwashing compositions are amylolytic enzymes.

The amylolytic enzymes for use in the present invention can be those derived from bacteria or fungi. Preferred amylolytic enzymes are those prepared and described in British Patent Specification N° 1,296,839, cultivated from the strains of *Bacillus licheniformis* NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11 945, ATCC 8480 and ATCC 9945 A. Examples of such amylolytic enzymes are amylolytic enzymes produced and distributed under the trade

name of SC-95® or Termamyl® by Novo Industri A/S, Copenhagen, Denmark. These amylolytic enzymes are generally presented as granules and may have enzyme activities of from about 2 to 10 Maltose units/milligram.

The amylolytic activity can be determined by the method as described by P. Bernfeld in "Method of Enzymology", Vol. I (1955), page 149.

The composition of the invention preferably also contains a proteolytic enzyme.

Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*, such as the commercially available subtilisins Maxatase® supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase®, supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of *Bacillus* having maximum activity throughout the pH range of 8-12, being commercially available from Novo Industri A/S under the registered trade names of Esperase® and Savinase®. The preparation of these and analogous enzymes is described in British Patent Specification N° 1,243,764.

Another suitable protease useful herein is a fairly recent commercial product sold by Novo Industri A/S under the trade name Durazym®, as described in WO-A-89/06279. The enzymes can be presented as granules, e.g. marumes, prills, T-granules etc., and may have enzyme activities of from about 500 to 1700 glycine units/milligram. The proteolytic activity can be determined by the method as described by M.L. Anson in "Journal of General Physiology" Vol. 22 (1933), page 79 (one Anson Unit/g = 733 Glycine Units/milligram). For convenient reasons enzyme preparations, are also commercially supplied as liquids or slurries e.g. Termamyl 300 L, Savinase 16.0 L, Savinase 16.0 SL.

All these enzymes can each be present in a weight percentage amount of from 0.2 to 5% by weight, such that for amylolytic enzymes the final composition will have amylolytic activity of from 10^2 to 10^6 Maltose units/kg, and for proteolytic enzymes the final composition will have proteolytic enzyme activity of from 10^6 to 10^9 Glycine Units/kg.

Enzyme granules containing only minor proportions, e.g. less than 30%, particularly not more than 10% by weight, of chloride to substantially nil, are preferably used in the compositions of the invention.

The Encapsulated Bleach Particles

Encapsulation techniques are known for both peroxygen and chlorine bleaches. US Patent Specification N° 4,126,573 to Johnston, for example, shows the encapsulation of a peroxyacid bleach with a water-soluble surfactant compound.

Several patents teach the use of coatings derived from fatty acids, such as US Patent N° 4,327,151 to Mazzola, which discloses an encapsulated bleaching agent having an inner coating of a fatty acid and a microcrystalline wax, and an outer coating of a fatty acid and Pluronic surfactants, and US Patent N° 3,983,254 to Alterman, which shows a method of encapsulating bleaching agents with fatty acids and alkali metal salts of fatty acids. Other encapsulated bleaches are also known. For example, US Patent N° 4,279,764 to Brubaker shows encapsulation of a mixture of an organic nitrogen-containing halogen bleaching agent, an N-H-containing compound, and a soluble inorganic hydratable salt. US Patent N° 3,036,013 to Jaszka teaches encapsulated calcium hypochlorite bleach.

The coatings can be applied in a variety of well-known methods including tumbling the coating and coated compound in a rolling mill, spraying a solution or suspension of the coating into a fluidized bed of the compound to be coated, precipitating the coating from a solvent on to the compound to be coated which is in suspension in the solvent, etc.

In the last few years, encapsulation technology has so progressed that chlorine or peroxygen bleach encapsulates of excellent stability can be produced. One of these improved technologies uses a wax coating and is described in EP-A-0,436,971 and in Applicant's European Patent Application EP-A-0 510 761. The problem, however, is that even a slight leakage would lead to enzyme degradation as explained before.

Still, a preferred encapsulated bleach particle for use in the present invention is that as described in the above-mentioned European patent applications, comprising 35-55% by weight of the particle of a single coat of paraffin wax and 45-65% by weight of a core of a chlorine or peroxygen bleach compound, the paraffin wax having a melting point of between 35°C and about 50°C, preferably from 40°C to 50°C, and having penetration values of from 10 to 60 mm at 25°C.

The bleach to be encapsulated in the coating may be a chlorine- or bromine-releasing agent or a peroxygen compound. Among suitable reactive chlorine- or bromine-oxidizing materials are heterocyclic N-bromo and N-chloro imides such as trichloroisocyanuric, tribromoisocyanuric, dibromoisocyanuric and dichloroisocyanuric acids, and salts thereof with water-solubilizing cations such as potassium and sodium. Hydantoin compounds such as 1,3-dichloro-5,5-dimethyl-hydantoin are also quite suitable.

Dry, particulate, water-soluble anhydrous inorganic salts are likewise suitable for use herein such as lithium, sodium or calcium hypochlorite and hypobromite. Chlorinated trisodium phosphate is another core material. Chloroisocyanurates are, however, the preferred bleaching agents. Potassium dichloroisocyanurate is sold by Monsanto Company as ACL-59®. Sodium dichloroisocyanurates are also available from Monsanto as ACL-60®, and in the dihydrate form,

from the Olin Corporation as Clearon CDB-56®, available in powder form (particle diameter of less than 150 microns); medium particle size (about 50 to 400 microns); and coarse particle size (150-850 microns). Very large particles (850-1700 microns) are also found to be suitable for encapsulation.

Organic peroxy acids or the precursors thereof may also be utilized as the bleach core. The peroxyacids usable in the present invention are solid and, preferably, substantially water-insoluble compounds. By "substantially water-insoluble" is meant herein a water-solubility of less than about 1% by weight at ambient temperature. In general, peroxyacids containing at least about 7 carbon atoms are sufficiently insoluble in water for use herein.

Typical monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxyacids such as:

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- α -naphthoic acid;
- (ii) aliphatic and substituted aliphatic monoperoxy acids, e.g. peroxy lauric acid and peroxy stearic acid;
- (iii) phthaloyl amido peroxy caproic acid (PAP).

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryl diperoxy acids, such as:

- (iv) 1,12-diperoxydodecanedioic acid (DPDA);
- (v) 1,9-diperoxyazelaic acid;
- (vi) diperoxybrassylic acid: diperoxysebacic acid and diperoxyisophthalic acid;
- (vii) 2-decyldiperoxybutane-1,4-dioic acid.

Peroxyacid bleach precursors are well known in the art. As non-limiting examples can be named N,N,N',N'-tetraacetyl ethylene diamine (TAED), sodium nonanoyloxybenzene sulphonate (SNOBS), sodium benzyloxybenzene sulphonate (SBOBS) and the cationic peroxyacid precursor (SPCC) as described in US Patent Specification 4,751,015.

Inorganic peroxygen-generating compounds may also be suitable as cores for the particles of the present invention. Examples of these materials are salts of monopersulphate, perborate monohydrate, perborate tetrahydrate, and percarbonate.

If desirably a bleach catalyst, such as the manganese complex, e.g. Mn-Me TACN, as described in EP-A-0458397, or the sulphonimines of US Patents 5,041,232 and 5,047,163, is to be incorporated, this can be presented in the form of a second encapsulate separately from the bleach capsule.

For chlorine bleaches the amount of encapsulates used in the compositions of the invention may vary within the range of about 0.5% to about 3% as available chlorine (Avcl). For peroxygen bleaching agents a suitable range will be from 0.5% to 3% avO (available oxygen).

The Reducing Agent

Reducing agents useful to prevent the appearance of an enzyme-deactivating concentration of oxidant bleach compound include reducing agent that can substantially reduce Cl_2 , HClO and other oxidizing chlorine-containing compositions to Cl^- ions or can substantially reduce hydrogen peroxide or peroxy acid bleaches to unoxidized species. The reducing agent should not damage the object or material to be cleaned or substantially chemically change the enzyme, or other cleaning composition components such as the detergent, builder, etc.

Useful reducing agents include reducing sulphur-oxy acids and salts thereof. Most preferred for reasons of availability, low cost, and high performance are the alkali metal and ammonium salts of sulphuroxy acids including ammonium sulphite $((\text{NH}_4)_2\text{SO}_3)$, sodium sulphite (Na_2SO_3) , sodium bisulphite (NaHSO_3) , sodium metabisulphite $(\text{Na}_2\text{S}_2\text{O}_5)$, potassium metabisulphite $(\text{K}_2\text{S}_2\text{O}_5)$, lithium hydrosulphite $(\text{Li}_2\text{S}_2\text{O}_4)$, etc., sodium sulphite being particularly preferred.

Another useful reducing agent, though not particularly preferred for reasons of cost, is ascorbic acid. These reducing agents must be used at sufficient amounts effective to scavenge the chlorine or oxidizing bleach leakage. It will be appreciated that these amounts may vary from case to case depending on the type and quality of the encapsulated bleach particles, but normally a range of about 0.01% to about 0.5% by weight, preferably from about 0.02% to about 0.2% by weight, will be sufficient. An amount lower than 0.01% may not be effective and an amount higher than 0.5% may not be necessary and, besides, in the case of sodium sulphite, is not wanted because of its smell.

Optional Ingredients

Optional ingredients are, for example, the well-known enzyme stabilizers such as the polyalcohols, e.g. glycerol, and borax; anti-scaling agents; crystal-growth inhibitors, threshold agents; thickening agents; perfumes and dyestuffs and the like.

A small amount of low- to non-foaming nonionic surfactant, which includes any alkoxylated nonionic surface-active agent wherein the alkoxy moiety is selected from the group consisting of ethylene oxide, propylene oxide and mixtures

thereof, is preferably used to improve the detergency and to suppress excessive foaming due to some protein soil. However, an excessive proportion of nonionic surfactant should be avoided. Normally, an amount of 0.1 to 7% by weight, preferably from 0.5 to 5% by weight, is quite sufficient.

Examples of suitable nonionic surfactants for use in the invention are the low- to non-foaming ethoxylated propoxylated straight-chain alcohols of the Plurafac® RA series, supplied by the Eurane Company; of the Lutensol® LF series, supplied by the BASF Company; of the Triton® DF series, supplied by the Rohm & Haas Company; and Sympconics, supplied by the ICI Company.

Another optional but highly desirable additive ingredient with multi-functional characteristics, particularly in non-phosphate compositions, is from 1% to 15%, preferably about 5% by weight, of a polymeric material having a molecular weight of from 1,000 to 2,000,000, and which can be a homo- or co-polymer of acrylic acid, maleic acid, or salt or anhydride thereof, vinyl pyrrolidone methyl- or ethyl-, vinyl ethers and other polymerizable vinyl monomers. Preferred examples of such polymeric materials are polyacrylic acid or polyacrylate; polymaleic acid or polyacrylate; polymaleic acid/acrylic acid copolymer; 70:30 acrylic acid/hydroethyl maleate copolymer; 1:1 styrene/maleic acid copolymer; isobutylene/maleic acid and diisobutylene/maleic acid copolymers; methyl- and ethylvinylether/maleic acid copolymers; ethylene/maleic acid copolymer; polyvinyl pyrrolidone; and vinyl pyrrolidone/maleic acid copolymer. These polymers are believed to function as co-builders, although under certain conditions they may also function as main builders.

The compositions of the present invention may also comprise, and preferably do, a thickener, for example a polymer such as a suitable acrylate, methacrylate (or copolymer thereof) or a cellulose such as hydroxymethyl cellulose. Typical inclusion levels of thickener are from 0.1% to 10%, e.g. from 0.5% to 5% by weight of the total composition.

Buffering agents may also be necessary to adjust and maintain the alkalinity and pH of the composition at the desired level. These are, for example, the alkali metal carbonates, bicarbonates and borates. Also sodium and/or potassium hydroxide may be used.

The invention may be more fully understood by way of the following illustrating Examples.

EXAMPLE I

The following aqueous liquid automatic dishwashing composition was prepared:

Composition I	% by weight
Carbopol® 941	1.50
NaOH (pellets)	0.80
Borax	3.00
Glycerol	6.00
Polymer (Sokalan® CF7)	5.00
Sodium citrate	30.00
Sodium sulphite	0.04
Chlorine bleach capsules 1)	4.30
Proteolytic enzyme (Savinase® 16.0L)	0.30
Amylase (Termamyl® 300 L)	0.30
Water	to 100.00 (abt. 49%).

1) The chlorine bleach capsules used herein comprise about 50% of Na-DCCA core and 50% of a paraffin wax coating, giving approx. 1.20% avCl. (see EP-A-0.436.971).

To aim for maximum enzyme activity directly after completing the processing steps, the order of addition during manufacture should be that the sodium sulphite is added as near as possible to the addition of the bleach encapsulation and definitely before the enzymes.

Enzyme stability of the composition is quite satisfactory.

When a similar composition was prepared containing 20% of sodium citrate, resulting in a water content of approximately 59% by weight, a substantial decrease of enzyme stability was observed.

Composition I was tested in a Miele 595SC dishwashing machine at a temperature of 55°C, using water of 14°FH. The cleaning results compared with the commercial Dutch products "Sun" Liquid and "Sun-Progress" are tabulated below.

Miele 595SC 55°C 14°FH

	Sun Liquid	Sun-Progress	Composition I
5			
	Porcelain plates		
	- potato	75	2
10	- custard	75	69
	- spinach	0	0
	Steel plates		
15	- potato	82	1
	- custard	97	72
			9
			82
			1)
	Potato pan		
20	- bottom	69	7
	- rim	78	18
	average	73	12
25	Custard spoon	50	17
			30
	Lipstick		
30	- cup	1.1	3.6
	- tumbler	1.2	3.7
	average	1.1	3.7
	Egg fork	1.2	1.1
35	Milk Glass	1.0	1.0
	Bleaching		
	Tea		
40	- cups	1.0	1.0
	- saucers	1.0	1.0
	- spoons	1.1	1.1
	average	1.0	1.0
45	Coffee		
	- cups	1.0	1.0
			1.7
			1.6
			1.6
			1.4
			1.0
			2)
			1.2
			1.0
			1.3
			1.2
			1.0
50			
	- Measurements		
55	- pH main wash	11.0	10.0
			8.5

- pH final rinse end	9.3	9.2	8.7
- FH Permanent	16.3	16.1	16.7
- FH Temporary	4.7	5.1	4.2

1) Residual Soil (%)

2) 4 point scale. 1-Complete removal, 4-No removal at all

EXAMPLE II

The effect of varying the nominal water content on Savinase and Amylase storage stability (in %) in a mechanical dishwashing liquid of base formulation given in Example I is shown in Figures 1 and 2, respectively.

Fig. 1 - The residual activity (%) of Savinase on the vertical axis is plotted against the nominal water content (%) by weight) of the liquid product after 5.5 weeks' storage at room temperature (—+—) and at 37°C (—•—).

Fig. 2 - The residual activity (%) of Amylase on the vertical axis is plotted against the nominal water content (%) by weight) of the liquid product after 5.5 weeks' storage at room temperature (—+—) and at 37°C (—•—).

The figures show clear improvement of enzyme storage stability in compositions containing less than 55% water. Especially Fig. 1 shows the dramatic drops of Savinase residual activity in compositions containing more than 55% water.

EXAMPLE III

Three aqueous liquid cleaning compositions comprising the following ingredients were prepared with varying amounts of sulphite.

Composition III	% by weight
Carbopol® 941	1.50
NaOH pellets	0.80
Borax	3.00
Glycerol	6.00
Polymer (Sokalan® CP7)	5.00
Sodium citrate	30.50
Sodium sulphite	0.00 - 0.04 - 0.10
MPS bleach capsules 1)	5.00
Proteolytic enzyme (Savinase® 16.0L)	0.30
Amylase (Termamyl® 300 L)	0.30
Water	to 100.00 (approx. 47%).

1) The MPS bleach capsules used herein are encapsulates comprising potassium monopersulphate (50% by weight) as the core bleach material provided with 50% by weight of a paraffin wax coating and prepared according to the method as described in EP-A-0,436,971.

These compositions were stored for 6 weeks at 37°C, whereafter the residual activities of Savinase and Termamyl were determined.

Savinase residual activity (%)

with 0.00% sulphite = 30%

with 0.04% sulphite = 80%

with 0.10% sulphite = 75%

Amylase (Termamyl) residual activity (%)

with 0.00% sulphite = 0%

with 0.04% sulphite = 95%

with 0.10% sulphite = 95%

These results demonstrate that low water level alone does not result in enzyme storage stability and that even at water level below 55% the presence of sulphite is essential.

EXAMPLE IV

This Example shows enzyme stability as a function of sulphite level in an accelerated storage test. The experiments were carried out with the formulations of Example I with varying levels of sodium sulphite. The compositions were stored at 50°C for 6 hours. The results are tabulated below.

Sulphite level (%)	Residual Activity (%)	
	Savinase	Amylase
0	0	0
0.02	4	5
0.04	5	7.5
0.10	30	37.5
0.20	67	82.5

Claims

1. Aqueous liquid cleaning composition comprising a detergency builder, an enzyme, encapsulated bleach particles and a reducing agent, characterized in that the composition has a water content of from 10% to not more than 55% by weight and the reducing agent is present in an amount of from 0.01 to 0.5% by weight.
2. A composition according to Claim 1, characterized in that said water content is not more than 50% by weight.
3. A composition according to Claim 1 or 2, characterized in that the amount of reducing agent is from 0.02 to 0.2% by weight.
4. A composition according to Claim 1, 2 or 3, characterized in that it has a pH of from 5.0 to 10.5.
5. A composition according to any of the preceding Claims 1-4, characterized in that the reducing agent is sodium sulphite.
6. A composition according to any of the preceding Claims 1-5, characterized in that it comprises an amylolytic enzyme.
7. A composition according to any of the preceding Claims 1-5, characterized in that it comprises a proteolytic enzyme.
8. A composition according to Claim 6 or 7, characterized in that it comprises a mixture of amylolytic and proteolytic enzymes.

Patentansprüche

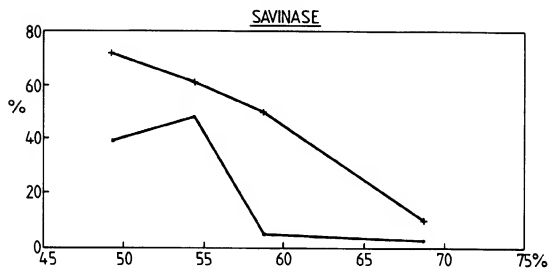
1. Wässrige flüssige Reinigungszusammensetzung, enthaltend einen Waschkraftbuilder, ein Enzym, verkapselte Bleichmittelteilchen und ein Reduktionsmittel, dadurch gekennzeichnet, daß die Zusammensetzung einen Wassergehalt von 10 bis nicht mehr als 55 Gewichtsprozent aufweist und das Reduktionsmittel in einer Menge von 0,01 bis 0,5 Gewichtsprozent vorhanden ist.
2. Eine Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der Wassergehalt nicht mehr als 50 Gewichtsprozent beträgt.
3. Eine Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Menge des Reduktionsmittels

von 0,02 bis 0,2 Gewichtsprozent beträgt.

4. Eine Zusammensetzung nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß sie einen pH-Wert von 5,0 bis 10,5 aufweist.
5. Eine Zusammensetzung nach irgendeinem der vorstehenden Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Reduktionsmittel Natriumsulfit ist.
6. Eine Zusammensetzung nach irgendeinem der vorstehenden Ansprüche 1 bis 5, dadurch gekennzeichnet, daß sie ein amylolytisches Enzym enthält.
7. Eine Zusammensetzung nach irgendeinem der vorstehenden Ansprüche 1 bis 5, dadurch gekennzeichnet, daß sie ein proteolytisches Enzym enthält.
8. Eine Zusammensetzung nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß sie eine Mischung von amylolytischen und proteolytischen Enzymen enthält.

Revendications

1. Composition de nettoyage aqueuse liquide comprenant un adjuvant de détergence, une enzyme, des particules de blanchiment encapsulées et un agent de réduction, caractérisée en ce que la composition a une teneur en eau de 10% à pas plus de 55% en poids et l'agent de réduction est présent en une quantité de 0,01 à 0,5% en poids.
2. Composition selon la revendication 1, caractérisée en ce que ladite teneur en eau n'est pas plus de 50% en poids.
3. Composition selon la revendication 1 ou 2, caractérisée en ce que la quantité de l'agent de réduction va de 0,02 à 0,2% en poids.
4. Composition selon la revendication 1, 2 ou 3, caractérisée en ce qu'elle a un pH de 5,0 à 10,5.
5. Composition selon l'une quelconque des revendications précédentes 1 à 4, caractérisée en ce que l'agent de réduction est le sulfite de sodium.
6. Composition selon l'une quelconque des revendications précédentes 1 à 5, caractérisée en ce qu'elle comprend une enzyme amylolytique.
7. Composition selon l'une quelconque des revendications précédentes 1 à 5, caractérisée en ce qu'elle comprend une enzyme protéolytique.
8. Composition selon la revendication 6 ou 7, caractérisée en ce qu'elle comprend un mélange d'enzymes amylolytique et protéolytique.

Fig.1.*Fig.2.*